

WO2004050561

Publication Title:

REACTIVE FILTRATION

Abstract:

14b2 Abstract of WO2004050561

In one embodiment, a reactive filtration method includes continuously regenerating a reactive filter media (22 or 76) while simultaneously filtering contaminants from fluid flowing through the filter media (22 or 76). In one embodiment, regenerating the reactive filter media (22 or 76) comprises mixing metal granules with the filter media (22 or 76) and agitating the mixture. In another embodiment, regenerating the reactive filter media (22 or 76) comprises introducing a metal in the fluid flowing through the filter media (22 or 76) and agitating the filter media (22 or 76). In one embodiment, a method for removing phosphorus, arsenic or a heavy metal from water includes introducing a metal salt reagent into the water at a molar ratio of 5:1 to 200:1 to the phosphorous or the arsenic in the water and passing the water through a bed of moving sand (22 or 76).

Data supplied from the esp@cenet database - Worldwide

Courtesy of <http://v3.espacenet.com>

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
17 June 2004 (17.06.2004)

PCT

(10) International Publication Number
WO 2004/050561 A1

(51) International Patent Classification⁷: **C02F 1/28**, 1/52,
B01J 20/06, 20/32, 20/34, B01D 24/28, 24/36, 24/46

(21) International Application Number:
PCT/US2003/040056

(22) International Filing Date: 2 December 2003 (02.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/430,756 4 December 2002 (04.12.2002) US

(71) Applicant: **IDAHO RESEARCH FOUNDATION, INC.**
[US/US]; Morrill Hall 103, University of Idaho, Moscow,
ID 83844-4061 (US).

(72) Inventors: **MOLLER, Greg**; 215 North Van Buren,
Moscow, ID 83843 (US). **KORUS, Roger**; 1038 Virginia
Ave., Moscow, ID 83843 (US). **NEWCOMBE, Remy**;
3665 North Scotch Pine Lane #1, Coure D'Alene, ID 83815
(US). **BRACKNEY, Kevin**; 838 Lynn Ave., Moscow, ID
83843 (US). **HART, Brian**; 696 Styner Ave., Moscow, ID
83843 (US). **KELLER, Gary**; 2614 South Third Street
Plaza, Omaha, NE 86106 (US).

(74) Agent: **ORMISTON, Steven, R.**; Ormiston & McKinney,
PLLC, P.O. Box 298, 802 W. Bannock, Suite 400, Boise,
ID 83701-0298 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE,
SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC,
VN, YU, ZA, ZM, ZW.

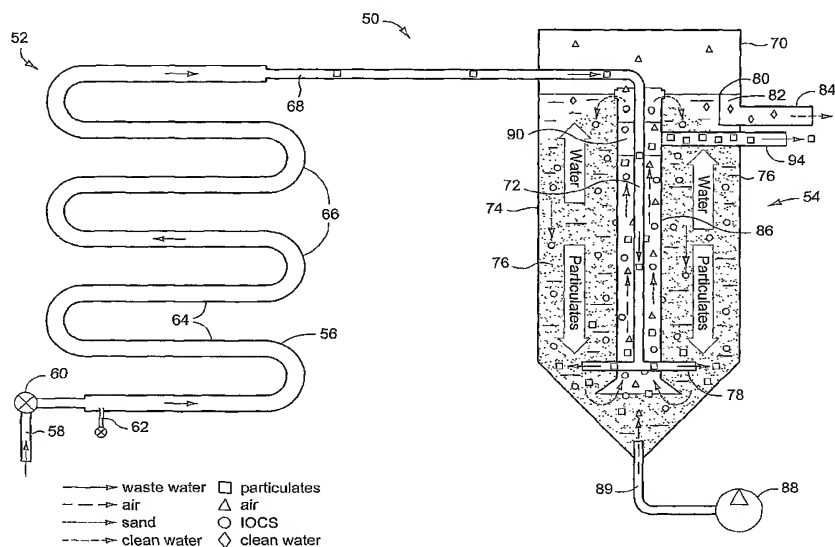
(84) Designated States (*regional*): ARIPO patent (BW, GH,
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,
SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted
a patent (Rule 4.17(ii)) for the following designations AE,
AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH,
CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI,*

[Continued on next page]

(54) Title: **REACTIVE FILTRATION**



(57) **Abstract:** In one embodiment, a reactive filtration method includes continuously regenerating a reactive filter media (22 or 76) while simultaneously filtering contaminants from fluid flowing through the filter media (22 or 76). In one embodiment, regenerating the reactive filter media (22 or 76) comprises mixing metal granules with the filter media (22 or 76) and agitating the mixture. In another embodiment, regenerating the reactive filter media (22 or 76) comprises introducing a metal in the fluid flowing through the filter media (22 or 76) and agitating the filter media (22 or 76). In one embodiment, a method for removing phosphorus, arsenic or a heavy metal from water includes introducing a metal salt reagent into the water at a molar ratio of 5:1 to 200:1 to the phosphorous or the arsenic in the water and passing the water through a bed of moving sand (22 or 76).

WO 2004/050561 A1



GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL,

PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

REACTIVE FILTRATION

BACKGROUND

[0001] Phosphorus exists in waters as dissolved ortho-phosphate, polyphosphate, and complex organo-phosphorus compounds. In typical phosphorus-containing waste waters, such as the secondary or tertiary effluents of municipal waste water treatment plants, there is a dissolved fraction of phosphorus compounds, primarily in the form of ortho-phosphate and polyphosphates, and a suspended fraction of micro-particulate phosphorus-containing solids. Trace levels of arsenic are sometimes found in some sources of drinking water and in higher concentrations in some waste waters. Arsenic can occur in natural waters as reduced arsenite, As(III), or oxidized arsenate, As(V).

[0002] Several methods are currently utilized for the removal of phosphorus compounds, arsenic, and other contaminants from waste water. Micro-particulate and other solid contaminants are typically removed by filtration using a solid media such as sand, and sedimentation, where solid contaminants with higher densities than water are allowed to settle. Dissolved contaminants are typically removed by flocculation and sorption. In flocculation, metal salt solutions are mixed with waste water to precipitate the contaminant out of solution, where it can then be removed through filtration or sedimentation. In sorption, contaminated waste water is passed through a stationary filtration media, typically iron oxide coated sand, having a partially charged cationic boundary layer that is reactive with a target contaminant dissolved in the waste water.

[0003] In conventional fixed-bed filtration systems, filtration media can quickly lose its filtration efficiency as the interstitial spaces between the particles of the filtration media become saturated with micro-particulate and solid contaminants. Thus, the filtration media must be flushed or replaced, which tends to be costly and time intensive. Additionally, the filtration process must be stopped while the filtration media is being flushed or replaced.

[0004] Moving-bed filtration devices seek to mitigate these limitations by utilizing processes that remove micro-particulate and solid contaminants from the filtration media while simultaneously filtering water. These moving-bed filtration

devices still have a disadvantage in that they do not remove dissolved contaminants from waste water.

[0005] U.S. Patent No. 5,369,072 to Benjamin et al. describes methods of preparing iron-oxide coated sand to be used as a filtration media in either fixed-bed or moving-bed systems to remove both solid and dissolved contaminants from waste water. When such a filtration media is used in a fixed-bed system, there remains the disadvantage of having to flush or replace the filter media on a regular basis to remove the solid contaminant waste. Although the use of this media in a moving-bed system may overcome these disadvantages, it does not overcome a disadvantage common to the use of the described iron oxide coated sand in either system. That is, the reactive surface of the iron oxide coated sand becomes saturated with adsorbed contaminants, and therefore needs to be either replaced or regenerated. Benjamin states that the adsorbed contaminant can be desorbed by treating the saturated filtration media with a solution with a pH range that is known to desorb the specific contaminant ion from the specific adsorbing surface. Therefore, in either a fixed-bed or moving-bed system, filtration of water must stop to allow the filtration media to be rinsed with pH solution.

[0006] Environmental concerns and increasingly stricter government regulations have many industries searching for cost-effective and efficient water-treatment solutions. Additionally, there is a recognized need to be able to filter out water contaminants that exist in what may be considered trace amounts. For example, the removal capability of conventional coagulation-precipitation methods drop off significantly at contaminant levels lower than 500 parts per billion (ppb). However, science has recognized that ambient phosphorus levels in water greater than 10-20 ppb can lead to eutrophication. The U.S. Environmental Protection Agency is pushing for lower limits of phosphorus in effluents. Currently, the EPA estuarine water criteria for total phosphorus is 0.10 mg/L. High volume dischargers are experiencing a reduction in the levels allowed in their regulatory permits.

DESCRIPTION OF THE DRAWINGS

[0007] Fig. 1 illustrates a moving bed particle filtration system that may be used to implement various embodiments of the invention.

[0008] Fig. 2 illustrates a moving bed filtration system constructed according to one embodiment of the invention in which the waste water is pre-treated with a reagent.

DETAILED DESCRIPTION

[0009] Embodiments of the invention were developed in an effort to more efficiently remove contaminants from waste water by increasing flows through a filtration system, even when contaminants are present in relatively small amounts. "Waste water" as used in this Description and in the Claims means any water to be treated -- it is not necessarily highly contaminated water and may contain only trace amounts of phosphorus, arsenic, or other contaminants (organic or inorganic and in single or mixed solution).

[0010] Fig. 1 illustrates a moving-bed particle radial filtration system 10 that may be used to implement various embodiments of the invention. Referring to Fig. 1, waste water flows into a vertically oriented cylindrical treatment vessel 12 through an inlet pipe 14. Vessel 12 includes a filter chamber 16, a stem 18 and an expansion gravity settling chamber 20. Filter chamber 16 contains a bed of sand 22, iron oxide coated sand, sand and iron granules or another suitable filter media. Inlet pipe 14 extends down into filter chamber 16. Waste water is discharged into sand 22 along the perforated lower part 24 of inlet pipe 14. Treated water flows out of filter chamber 16 through a perforated outer perimeter 26 into a sleeve 28 and is removed from vessel 12 through an outlet pipe 30. The perforations in the lower part 24 of inlet pipe 14 and the outer perimeter 26 of filter chamber 16 are screened as necessary to prevent sand from passing through the perforations.

[0011] The comparatively narrow stem 18 of vessel 12 connects filter chamber 16 with expansion chamber 20. A sludge removal port 32 is positioned near the bottom of expansion chamber 20. A recirculation pipe 34 extends from the bottom of filter chamber 16 to the top of expansion chamber 20. An air compressor 36 pumps air into recirculation pipe 34 at the bottom of filter chamber 16 causing a counterclockwise motion of air, water, sand and filtered particulates through vessel 12. A back flow preventer 38, such as a flapper valve, prevents materials in recirculation pipe 34 from flowing back into compressor 36. A flow control valve 39, sampling tube 40, sampling valve 42

and clean-out 43 on recirculation pipe 34, and a sight glass 44 in stem 18, may be provided if necessary or desirable.

[0012] In operation, waste water pumped into filter chamber 16 through inlet pipe 14 passes radially through sand 22 into sleeve 28 and flows out outlet pipe 30 as treated water. Sand 22 moves continuously down through vessel 12 under the influence of gravity. An aerated mixture of used sand and water flows from the bottom of filter chamber 16 back up to expansion chamber 20 through recirculation pipe 34 along with contaminants removed from the waste water. Air is vented to the atmosphere at the top of expansion chamber 20 to prevent pressurization of the system. The pressure head of water in sand 22 is kept such that some of the treated water flows from filter chamber 16 up through stem 18 into expansion chamber 20 to rinse contaminants from the used sand particles returning to expansion chamber 20. This rinse water, now carrying a high concentration of contaminants less dense than sand, is removed from chamber 22 and flows out through sludge removal port 32. In a preferred operation, the top of the sand bed for filtration is three fourths the height of filter chamber 16. Expansion chamber 20 and narrow stem 18 contain a dilute sand and water mixture that contains filtered particles that have been moved first to the bottom of sand 22 and circulated via pipe 34 into the water residing in expansion chamber 20. Water flow at inlet pipe 14, outlets 30 and 32 and recirculation pipe 34 can be balanced so that a preferred rate of 5-10% of the inlet water carrying contaminants is discharged through sludge removal port 32.

[0013] The system of Fig. 1 may be used to implement a process for continuously regenerating an iron oxide coated sand bed while simultaneously filtering contaminants from the incoming flow of waste water. The process creates and utilizes a reactive filter media that removes contaminants by filtering and by adsorption. A reactive filter media is any filter media with the additional capability of removing contaminants from waste water through chemical processes such as adsorption. The iron oxide coated sand bed, a reactive filter media, screens contaminants from the water and the reactive surfaces of the granules of sand adsorb contaminants from the water. In one embodiment, iron metal granules in proportions of 10-30% by volume in sand bed 22 provide a solid phase reactive surface of corroding iron metal as well as a source of dissolved iron such as salts of Fe (II) and Fe(III) that react with the sand in the

filter bed to create reactive iron oxide coated sand. The strongly reducing nature of water solutions with iron metal and sand mixtures can be useful for chemical reactions, such as the reductive degradation of organic solvents dissolved in contaminated water. Reduction potentials lower than -200 mV versus the standard hydrogen electrode can be observed with 30% iron:sand mixtures.

[0014] In an alternative embodiment, a reagent capable of creating a reactive surface on the filter media is added to the incoming flow of waste water at molar ratios such as 5:1 to 200:1 with the target contaminant. While it is expected that soluble forms of manganese, aluminum or other metals such as zinc and copper will provide suitable reagents, iron will typically be used as the reagent due to its proven reactivity with a variety of contaminants and its current widespread use in water treatment. Ferric chloride, for example, is a preferred reagent when phosphorus or arsenic is the target contaminant. In any particular water targeted for treatment, there may be alternate and competitive reactive pathways for the added active reagents. These pathways will be the result of the specific water chemistry in the waste water. For example, waste water with high levels of dissolved carbonate or phosphate can react with added iron salts in competition to the target contaminant such as arsenic. Molar ratios of Fe(III) to water arsenic in field studies have been in excess of 100:1. In these studies, inlet concentrations of arsenic in source water for drinking were reduced from approximately 40 parts per billion to less than 5 parts per billion treating at a rate of 10 gallon per minute in a pilot scale operation. However, other water types may have less alternate, competitive reactive pathways. It is preferred to field test to determine the optimal molar ratio for any particular treatment environment to ensure sufficient excess reagent is delivered to the reactive sand surface to form iron oxide coated sand. Additional considerations in reagent balancing direct efforts to minimizing reagent addition to ensure that the process effluents are not overly high in dissolved iron or other reagent, thereby creating an additional treatment or discharge concern. Excess reagent consumption will also undesirably increase the cost of operation of the process.

[0015] In the removal of dissolved and suspended phosphorus, field studies have demonstrated that successful high flow, low concentration removal occurs in this process in iron to phosphorous molar ratios of 5:1 to 40:1. It is preferred that the actual reagent dose is optimized to ensure near complete solution

reaction and saturation of all of the competing reactive pathways and allowing for residual iron in the solution to react with the sand bed. In some phosphorus contaminated test waste waters, optimizing the correct balance of conditions yields a preferred ratio of iron to phosphorus at 8:1. The metal salt reagent, ferric chloride in this example, reacts with the surface of the sand to form iron oxide coated sand (IOCS). IOCS provides a stationary phase removal pathway for water borne contaminants such as phosphorus and arsenic. Contaminants in the waste water are exposed as a "mobile" phase over the "stationary" (slowly moving) IOCS bed for high efficiency sorptive and ion exchange removal. The physical action of the moving sand abrades the surface of the sand granules, regenerating active sites for additional iron salt and water contaminant reactions. Hence, regenerated reactive sites for contaminant binding are continually presented to the flowing water. Abraded sand-iron-contaminant solids are removed by the screen filtering action of the sand bed. The treated water exits the sand filter bed with contaminants substantially removed, ready for discharge or post-treatment processing.

[0016] Sorption is the removal of undersaturated solutes from solution onto minerals. Sorbate is the species removed from solution and the sorbent is the solid onto which solution species are sorbed. There are three types of sorption: adsorption wherein solutes are held at the mineral surface as a hydrated species; absorption wherein solute is incorporated into the mineral structure at the surface; and ion exchange wherein an ion becomes sorbed to a surface by changing places with a similarly charged ion previously residing on the sorbent. Mineral surfaces, such as the silicates in sand, have fixed or acquired surface charges that can be modified by water chemistry such as pH and dissolved solutes such as iron salts that can complex with the surface charges of sand. As a result of fixed surface charges, a property of the mineral, and pH, a property of the water, mineral surfaces develop a point of zero net proton charge (PZNPC). The PZNPC is the pH at which net surface charge is zero. At lower pH than PZNPC, the net surface charge is positive and at higher pH, the net surface charge is negative. These surface charges allow attraction of oppositely charged anions or cations, respectively, from solution. Larger amounts of dissolved constituents, such as positively charged Fe(III) can be attracted to a negatively charged surface such as the silicates in sand to such a degree that the surface

becomes overall positively charged and therefore attractive to anions such as phosphate and arsenate. Silica, SiO_2 has a low PZNPC of 2, whereas iron oxyhydroxide, $\alpha\text{-FeOOH}$ has a PZNPC of 7.8, and iron hydroxide, $\text{Fe}(\text{OH})_3$ has a PZNPC of 8.5. Increasing quantities of iron oxide forming on a sand surface will increase the PZNPC of the sand grains such that net surface charge is positive and thereby attractive to anions such as phosphate and arsenate at higher pH levels of about 6-8. Most environmental waters, including drinking water and wastewaters exist at these circum-neutral pH levels. Hence, the selective addition of iron oxides to the sand creates a useful sorbent.

[0017] In a moving sand bed system such as the one shown in Fig. 1, concentrated contaminants, now in the form of filterable solid waste, are removed from the system through sludge removal port 32 via continuous rinsing in expansion chamber 18. This continuous rinsing and waste removal process is particularly important in the case of a hazardous material such as arsenic in drinking water. Rinse/waste water outflow, typically 5-10% of the incoming water, can be recycled and put back into the process following separation of the suspended solids by settling or clarification. In a fixed-bed system, in which the particulate filtrate remains on the sand and in the sand, the sand bed is periodically flushed or changed out to remove the concentrated contaminant waste.

[0018] Fig. 2 illustrates a novel moving bed filtration system 50 constructed according to one embodiment of the invention in which the waste water is pre-treated with a metal salt reagent. Referring to Fig. 2, filtration system 50 includes a pre-reactor system 52 and a reactive filter system 54. Waste water is pumped into the serpentine piping 56 of pre-reactor 52 through an inlet pipe 58 and flow control valve 60. A metal salt or other suitable reagent is introduced into serpentine piping 56 through a reagent inlet port 62 immediately downstream from inlet pipe 58. Preferably, serpentine piping 56 is substantially larger than inlet pipe 58 to slow the flow through piping 56 compared to inlet pipe 58. A slower flow increases the time available for the reagent to mix with the waste water and react with contaminants in the waste water. The waste water flow will be more turbulent near the transition from the smaller inlet pipe 58 to the larger serpentine piping 56. Introducing the reagent into this turbulent flow also helps mixing.

[0019] The waste water/reagent mix flows through straight-aways 64 and gentle bends 66 of serpentine piping 56. The waste water/reagent mix exits serpentine piping 56 into an outlet pipe 68 that takes the mix into reactive filter system 54. Prescribed overdosing introduces the reagent in sufficient quantities and concentrations to (1) allow for the co-precipitation and flocculation reactions between the reagent and the dissolved contaminants in pre-reactor system 52 to go to near completion to dilute levels where equilibrium and diffusion limited processes limit further reaction, (2) saturate competing reactive pathways with natural waters with reagent, and (3) leave enough excess reagent in the mix to activate the filter media in reactive filter system 54. The amount of excess reagent is determined by the reactive capacity of the influent solution and the desire to deliver excess reagent to the sand filtration bed for the continuous formation of iron oxide coated sand.

[0020] The comparatively slow flow through serpentine piping 56 allows for better coagulation of precipitates. The straight-aways 64 allow for less turbulent flow to enhance coagulation. Periodic gentle bends 66 introduce and maintain additional turbulent flow and introduce flow vortices to periodically mix the flowing solution. Preferably, the serpentine mixing array allows for a decrease in flow velocity for 2-8 minutes to allow for sufficient pre-reaction time. Design of the array needs to consider maintaining sufficient flow to prevent deposition of precipitation solids in the pre-reactor assembly. The actual length and diameter of serpentine piping 56 for most applications will result for an optimization of the required reaction time (usually 1-5 minutes), the desired flow rate, the space available at the site of deployment, and the presence of competing reactions in the treatment water.

[0021] The pre-treated waste water flows into the vertically oriented cylindrical treatment vessel 70 of reactive filtration system 54 through an inlet pipe 72. Inlet pipe 72 is positioned at the center of vessel 70. Vessel 70 includes a filter chamber 74 that contains a bed of sand 76 or another suitable filter media. Inlet pipe 72 extends down into filter chamber 74 to discharge the waste water into the lower portion of sand bed 76 through a perforated manifold 78. Waste water pumped into filter chamber 74 passes up through sand 76, over a baffle 80 near the top of filter chamber 74 as fully treated water, into a basin 82 and is removed from vessel 70 through an outlet pipe 84.

[0022] A recirculation tube 86 extends from the bottom to the top of filter chamber 74 at the center of vessel 70. Inlet pipe 72 extends down the center of recirculation tube 86. Inlet flow discharge manifold 78 extends out through openings in recirculation tube 86. An air compressor 88 pumps air into used sand and water at the bottom of vessel 70 through an air inlet pipe 89. The aerated mixture of used sand and water rises through recirculation tube 86 along with contaminants removed from the waste water up to a sand and particulate/water separator 90. Separator 90 represents generally any suitable separation device that may use, for example, physical separation, gravity separation, particle size separation, magnetic separation, membrane separation, or cyclonic separation. The sand removed from the mix by separator 90 is recycled back to filter chamber 74. The now highly contaminated waste water is removed through a sludge removal port 94. Sand 76 moves continuously down through vessel 70 under the influence of gravity.

[0023] Phosphorus exists in waters and waste waters as dissolved ortho-phosphate, polyphosphate and complex organo-phosphorus compounds. In typical phosphorus containing waste waters, such as the secondary or tertiary effluents of municipal waste water treatment plants, there is a dissolved fraction, primarily as ortho-phosphate (PO_4^{3-}) and poly-phosphates and as a micro-particulate or suspended fraction of phosphorous containing solids. Trace levels of arsenic are sometimes found in some sources of drinking water and in higher concentrations in some waste waters. Arsenic can occur in natural waters in the reduced arsenite, As(III) or oxidized arsenate, As(V) forms. Arsenate reacts with iron and aluminum salts to form insoluble compounds. Waters with arsenite contamination can be treated with an oxidizer such as chlorine to allow for further reaction with reactive metal salts. Ferric chloride or sulfate is typically used as a metal salt reagent to remove phosphorus and arsenic from water, although other salts and ferrous compounds can be used.

[0024] In the system described above, excess ferric iron enters sand bed 76 along with the particulate Fe-As or Fe-P solids and residual As or P in solution in the waste water. Ferric ions react with sand surfaces to form iron oxide coated sand (IOCS). IOCS sorbs residual solution As/P out of solution. The physical action of the moving sand abrades the surface of the sand granules, refreshing active sites for additional IOCS formation and Fe-As or Fe-P

reactions. Hence, fresh reactive sites for As/P binding are continually presented to the flowing water via microscopic erosion of the sand surface.

[0025] For phosphorus, ferric chloride is added at a preferred molar ratio of 5:1 to 40:1 with the phosphorus in the waste water. The pre-reactor system allows for a pre-reaction to form metal phosphate salts such as FePO_4 , Vivianite and humic-fulvic organic phosphorus solids that are amenable to filtration in the sand bed reactive filter system. Vivianite is a very thermodynamically stable compound that is rapidly formed in solutions of iron cations and phosphate. Excess iron salt reagent is passed unreacted into the sand bed where it binds to the surface of the sand to form iron coated sand, a phosphate and polyphosphate reactive surface. Metal cations will selectively bind to the silicate and other negatively charged groups on the solid sand surface. This binding will yield a partially charged cationic boundary layer on the iron coated sand surface that will be reactive with soluble ortho-phosphate and poly-phosphate. The mobile phase (treatment water) and stationary phase (iron coated sand) configuration of this process allows for near quantitative removal of phosphorus because diffusion processes are nearly eliminated in the dilute solution reactive pathway of this process. Testing has shown that this process can remove ortho-phosphate to less than detection limits (10 part per billion) at efficiencies greater than 99% and total phosphorus to less than 40 parts per billion at greater than 90% efficiency of removal from the original concentration.

[0026] The processes described above have been shown to produce iron arsenic solids that are classified non-hazardous by the Toxicity Characteristic Leaching Procedure (TCLP) directed by the Resource Conservation and Recovery Act (RCRA 42 U.S.C. s/s 6901 et seq.) and can be disposed in a landfill, and iron phosphate solids that may be used in agricultural applications as a low grade slow release fertilizer.

[0027] The reactive filter media are deployed in a moving bed to assist in continuous renewal of the reactive iron oxide layer. Movement may be accomplished, for example, by fluidizing or moving the bed using the fluid flow, by mechanical action such as augers or mixing bars, by acoustic action such as the application of ultrasonic waves or by physical transport using compressed air.

[0028] Other embodiments are possible. For example, the filter media can be any natural or synthetic, organic or inorganic substrate that can react with

dissolved iron to form a reactive oxide surface. The particle size of the filter media will be a size suitable for the level of filtration and flow desired. It is expected that the following inorganic materials will provide suitable filtration media: sand; silica beads or granules; high silicate glass; glass beads; glass sand; zeolite; mineral sands such as olivine, hematite, goethite; diatomaceous earth; iron oxyhydroxide granules; iron oxide granules; ceramic beads or granules; iron metal granules or beads; iron metal coated beads or granules; and synthetic or natural iron coated sand. It is expected that the following organic materials will provide suitable filtration media: polystyrene beads; polyethylene beads; modified cationic surface polymer beads; modified anionic surface polymer beads; mixed or pure polymer beads or granules; and polymer coated inorganic beads or granules. Some of these materials can have naturally occurring reactive sites that can be maintained or supplemented by the addition of active reagents such as ferric chloride solution. Because of the well known filtration properties of sand, its inexpensive use, its routine application in water treatment, its natural reactive silicate surface for inner sphere and outer sphere metal oxide binding to form iron oxide coated sand, and its abrasion properties, it is the preferred embodiment of an active filtration media in a moving bed process.

[0029] Suitable filtration media include corroding iron metal granules or ion exchange resins with the ability to bind iron compounds. Corroding iron metal granules allow for reductive processes that can be used to remove trace amounts of chlorinated solvents in water. Testing has shown that a 30% by volume iron-sand bed deployed in the system of Fig. 1 has a solution oxidation-reduction potential of -200 mV versus the standard hydrogen electrode. Typical deployments of static beds of iron granules or iron granules and sand suffer from loss of porosity or passivation of the reactive iron metal surface. The motion of a moving bed deployment allows for a continual refreshing of the iron metal surface and its associated chemically reactive sites as well as maintenance of filtration ability. A 98% efficiency has been demonstrated for removing phosphorus from contaminated discharge water originally containing 2 to 3 parts per million phosphorus.

[0030] In some circumstances, removing arsenic for example, it may be desirable to pre-oxidize the waste water to convert arsenite to the iron reactive

arsenate. Arsenite in natural solutions at circumneutral pH is non-ionic and therefore typically non-reactive in most treatment deployments. Pre-oxidation can be accomplished using conventional water oxidation operations such as chlorination, sonication or ozonation. The pre-oxidation operation can be part of a full water treatment process train and may be preceded or followed by other conventional water treatment processes such as filtration, aeration, chemical treatment, flocculation, clarification and others that may be required in the normal processing and disinfection of drinking water.

[0031] The present invention has been shown and described with reference to the foregoing exemplary embodiments. It is to be understood, however, that other forms, details, and embodiments may be made without departing from the spirit and scope of the invention which is defined in the following claims.

CLAIMS

What is claimed is:

1 1. A reactive filtration method, comprising continuously regenerating a
2 reactive filter media (22 or 76) while simultaneously filtering contaminants from
3 fluid flowing through the filter media (22 or 76).

1 2. The method of Claim 1, wherein regenerating the reactive filter
2 media (22 or 76) comprises mixing metal granules with the filter media (22 or 76)
3 and agitating the mixture.

1 3. The method of Claim 1, wherein regenerating the reactive filter
2 media (22 or 76) comprises introducing a metal salt reagent into the fluid flowing
3 through the filter media (22 or 76) and agitating the filter media (22 or 76).

1 4. The method of Claim 1, 2 or 3, wherein the fluid is waste water.

1 5. The method of Claim 4, wherein regenerating the reactive filter
2 media (22 or 76) comprises corroding a metal in the waste water flowing through
3 the filter media (22 or 76) and agitating the filter media (22 or 76).

1 6. The method of Claim 4, wherein regenerating the reactive filter
2 media (22 or 76) comprises introducing a metal salt reagent into the waste water
3 at a molar ratio of 5:1 to 200:1 with a target contaminant in the waste water.

1 7. A reactive filtration method, comprising continuously regenerating
2 an iron oxide coated sand bed (22 or 76) while simultaneously filtering
3 contaminants from waste water flowing through the sand bed (22 or 76).

1 8. The method of claim 7, wherein regenerating the sand bed (22 or
2 76) comprises mixing iron granules with sand and agitating the mixture.

1 9. The method of claim 7, wherein regenerating the sand bed (22 or
2 76) comprises introducing an iron salt reagent into the waste water flowing
3 through the sand bed (22 or 76) and agitating the sand.

1 10. The method of claim 9, wherein introducing iron into the waste
2 water comprises introducing a salt of Fe(II) or Fe(III) into the waste water.

1 11. A reactive filtration method, comprising passing waste water
2 through a moving mixture of sand (22 or 76) and metal granules.

1 12. A reactive filtration method, comprising introducing a metal ion into
2 waste water and passing the waste water through a bed of moving sand (22 or
3 76).

1 13. A method for removing phosphorus, arsenic, selenium or another
2 heavy metal from water, comprising:
3 introducing a metal salt reagent into the water at a molar ratio of 5:1 to
4 200:1 to the phosphorous, arsenic, selenium or other heavy metal in the water;
5 and
6 passing the water through a bed of moving sand (22 or 76).

1 14. A method for removing phosphorus according to Claim 13, wherein
2 introducing a metal salt reagent into the water at a molar ratio of 5:1 to 200:1 to
3 the phosphorous in the water comprises introducing a metal salt reagent into the
4 water at a molar ratio of 5:1 to 40:1 to the phosphorous in the water.

1 15. The method of claim 14, wherein introducing a metal salt reagent
2 into the water comprises introducing ferric chloride, ferrous chloride, ferric sulfate
3 or ferrous sulfate into the water at a molar ratio of 5:1 to 40:1 to the phosphorous
4 in the water.

1 16. A method for removing arsenic according to Claim 13, wherein
2 introducing a metal salt reagent into the water at a molar ratio of 5:1 to 200:1 to

3 the arsenic in the water comprises introducing a metal salt reagent into the water
4 at a molar ratio of 100:1 to 200:1 to the arsenic in the water.

1 17. The method of claim 16, wherein introducing a metal salt reagent
2 into the water comprises introducing ferric chloride, ferrous chloride, ferric sulfate
3 or ferrous sulfate into the water at a molar ratio of 100:1 to 200:1 to the
4 phosphorous in the water.

1 18. A reactive filtration method, comprising:
2 adding a metal salt reagent to the waste water in sufficient quantity and
3 concentration to allow precipitation reactions between the reagent and a
4 dissolved contaminant to go to at least near completion and to leave unreacted
5 reagent in the water;
6 flowing the waste water through a serpentine pipe (56) configured to
7 produce more turbulent flow through bends (66) in the pipe (56) and less
8 turbulent flow through straight-aways (64) in the pipe (66);
9 controlling the flow rate of waste water through the serpentine pipe (56) to
10 allow precipitation reactions between the reagent and a dissolved contaminant to
11 go to at least near completion while maintaining sufficient flow to inhibit
12 deposition of solids, precipitates or particulates in the serpentine pipe (56); and
13 then
14 flowing the waste water through a bed of moving filter media (22 or 76),
15 wherein unreacted metal salt reagent in the waste water reacts with the filter
16 media (22 or 76) to generate a reactive metal oxide or hydroxide coating on the
17 filter media (22 or 76) to adsorb dissolved contaminants remaining in the waste
18 water.

1 19. The method of claim 18, wherein the contaminant is phosphorus,
2 arsenic, selenium or another heavy metal and the metal salt reagent is ferric
3 chloride, ferrous chloride, ferric sulfate or ferrous sulfate and the filter media (22
4 or 76) is sand.

1 20. The method of claim 19, wherein the contaminant is phosphorous
2 and unreacted ferric chloride, ferrous chloride, ferric sulfate or ferrous sulfate in

3 the waste water entering the bed of moving sand (22 or 76) provides a molar
4 ratio of iron to phosphorus of 5:1 to 40:1.

1 21. The method of claim 19, wherein the contaminant is arsenic and
2 unreacted ferric chloride, ferrous chloride, ferric sulfate or ferrous sulfate in the
3 waste water entering the bed of moving sand (22 or 76) provides a molar ratio of
4 iron to phosphorus of 100:1 to 200:1.

1 22. The method of claim 19, wherein the contaminant is arsenic and
2 further comprising, before adding a metal salt reagent, oxidizing the waste water
3 to convert arsenite in the waste water to arsenate.

1 23. A filtration device (54), comprising:
2 a vessel (70);
3 a filtration chamber (74) within the vessel (70);
4 reactive filter media (76) in the filtration chamber (74);
5 a first inlet (72) through which waste water may be pumped into a lower
6 part of the filtration chamber (74) and up through the filter media (76);
7 a second inlet (89) through which air may be pumped into the lower part of
8 the filtration chamber (74);
9 a recirculation pipe (86) open to and extending vertically up from the
10 second inlet (89) such that an aerated mixture of water and filter media can flow
11 up through the recirculation pipe (86);
12 a separator (90) configured to remove the filter media (76) from an
13 aerated mixture of water and filter media flowing through the recirculation pipe
14 (86); and
15 an outlet (84) through which filtered water can be removed from the
16 filtration chamber (74).

1 24. The device of claim 23, wherein the reactive filter media (76)
2 comprises iron oxide coated sand.

1 25. The device of claim 23, wherein the reactive filter media (76)
2 comprises a mixture of sand and iron granules.

1 26. The device of claim 23, wherein the reactive filter media (76)
2 comprises a mixture of 10–30% iron granules by volume and sand.

1 27. The device of claim 23, wherein the recirculation pipe (86) extends
2 vertically up from the second inlet (89) to a top of the filter chamber (74) through
3 which filter media (76) exiting the separator may return to the filtration chamber
4 (74).

1 28. A filtration device, comprising a means for continuously
2 regenerating a reactive filter media (22 or 76) while simultaneously filtering
3 contaminants from fluid flowing through the filter media (22 or 76).

1 29. The device of Claim 28, wherein the means for regenerating the
2 reactive filter media (22 or 76) comprises a means for mixing corroding metal
3 granules with the filter media (22 or 76) and a means for agitating the mixture.

1 30. The device of Claim 28, wherein the means for regenerating the
2 reactive filter media (22 or 76) comprises a means for introducing a corroding
3 metal in the fluid flowing through the filter media (22 or 76) and a means for
4 agitating the filter media (22 or 76).

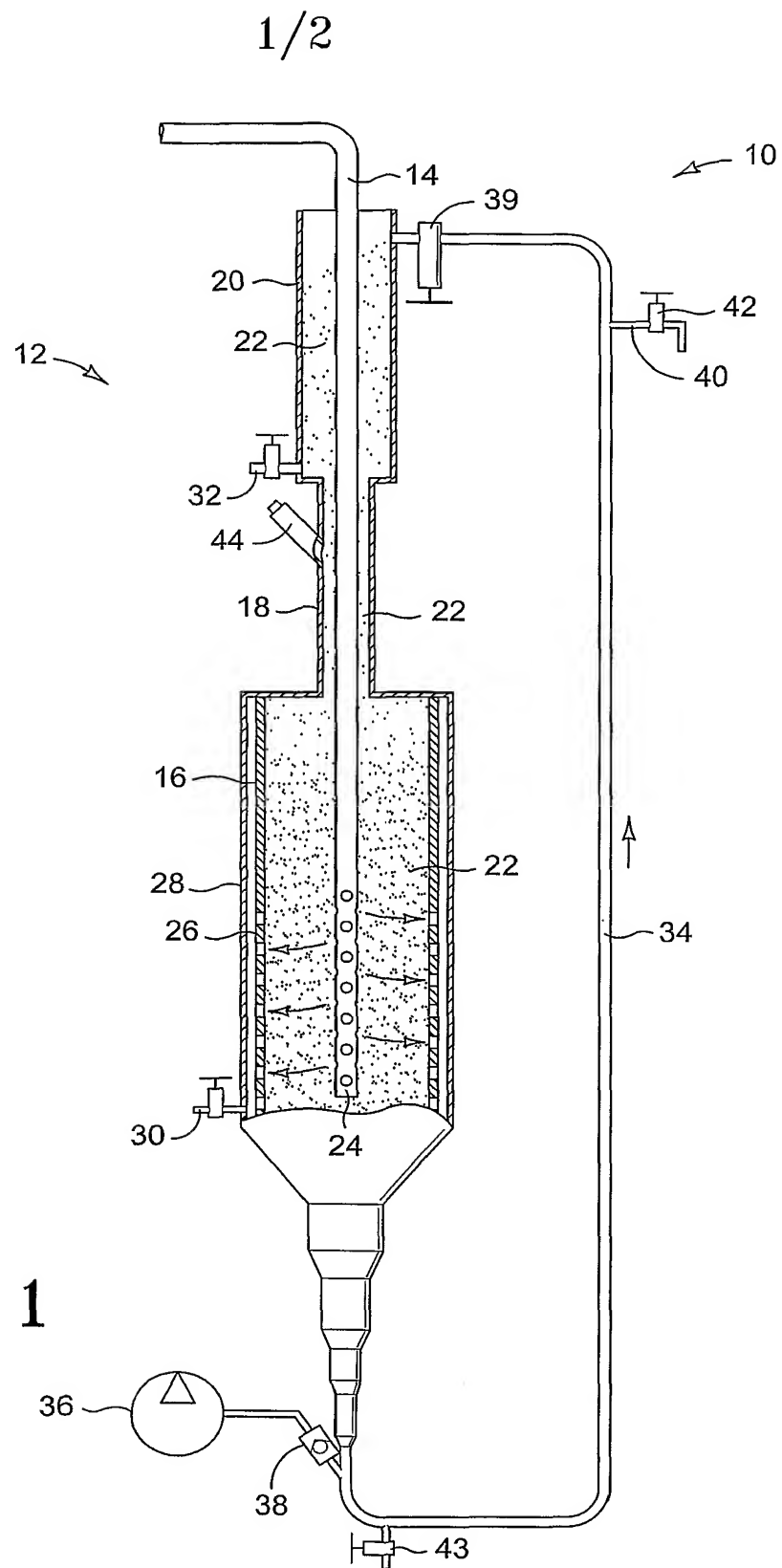


FIG. 1

2/2

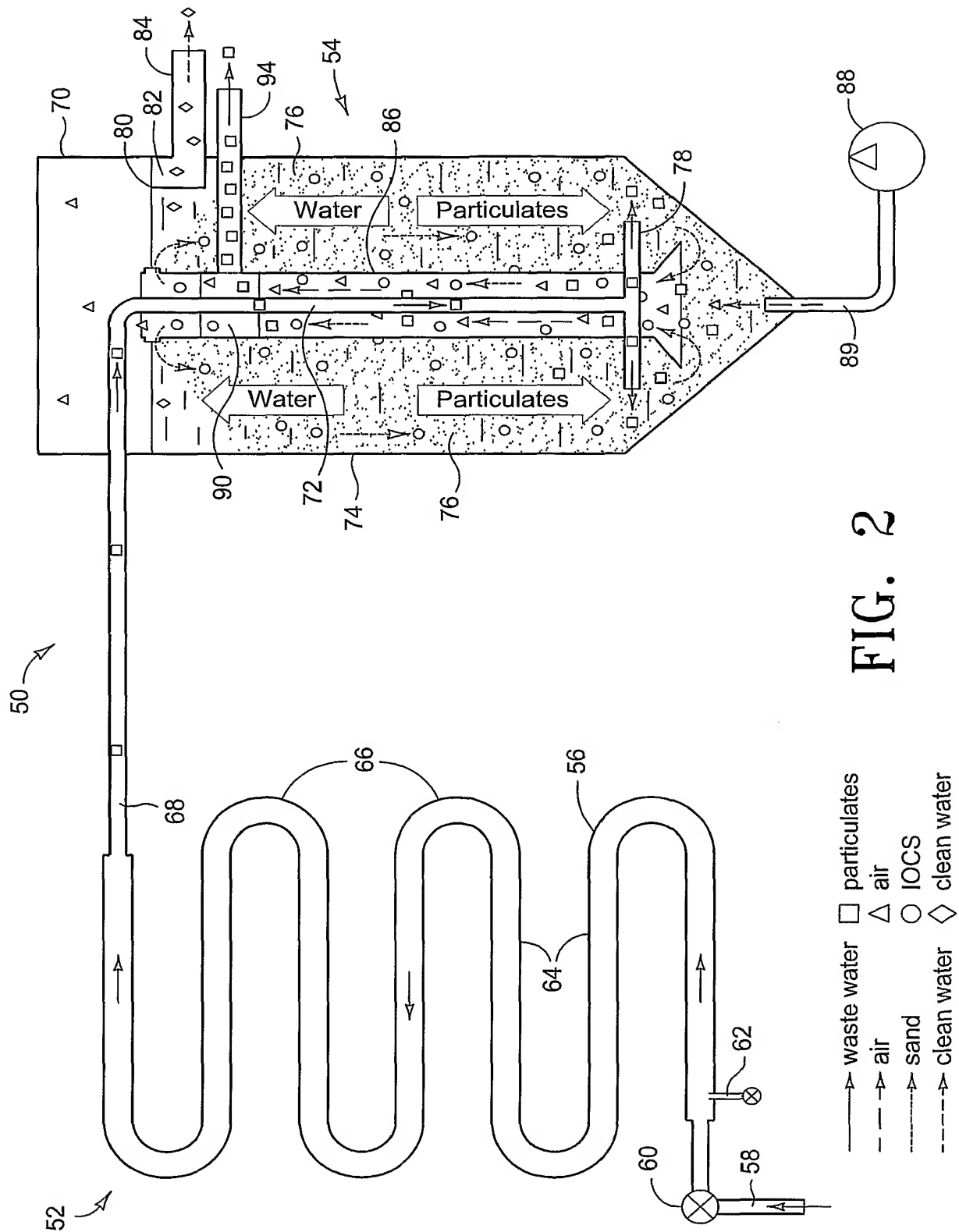


FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/40056

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C02F1/28 C02F1/52 B01J20/06 B01J20/32 B01J20/34
 B01D24/28 B01D24/36 B01D24/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F B01J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 471 277 A (C F BURGESS LAB INC) 1 September 1937 (1937-09-01) page 1, line 63-71,93-106 page 3, line 94-103 page 4, line 71-96 ----	1
X	US 6 132 623 A (NIKOLAIDIS NIKOLAOS P ET AL) 17 October 2000 (2000-10-17) claims 1,2,6 column 2, line 48-59 column 5, line 7-14,50-59 ----	1,2,11
X	DE 27 24 254 A (BBC BROWN BOVERI & CIE) 9 November 1978 (1978-11-09) claim 1; example 3 page 3, line 11 -page 4, line 3 ----- -/--	1-22



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
 E earlier document but published on or after the international filing date
 L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 O document referring to an oral disclosure, use, exhibition or other means
 P document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
 & document member of the same patent family

Date of the actual completion of the international search

27 April 2004

Date of mailing of the international search report

06/05/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Harf, J

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/40056

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 426 005 B1 (LARSSON HANS F) 30 July 2002 (2002-07-30) figure 1 column 2, line 1-20 column 5, line 44 -column 7, line 10 ----	23-30
X	US 4 126 546 A (HJELMNER ULF R ET AL) 21 November 1978 (1978-11-21) figure 1 column 1, line 51-66 column 3, line 29-38 ----	23-30
A	US 5 369 072 A (CHANG YU-JUNG ET AL) 29 November 1994 (1994-11-29) cited in the application column 3, line 46-64 column 4, line 29-39 column 6, line 1-4 column 9, line 17-22 column 10, line 40-44 column 14, line 55-58 ----	1-22
A	US 3 499 837 A (JAUNARAJIS KARLIS LAIMONIS) 10 March 1970 (1970-03-10) claims 1,10 column 2, line 34-48 column 2, line 57-64 column 3, line 61-69 ----	1-30
A	US 6 468 942 B1 (SANSALONE JOHN J) 22 October 2002 (2002-10-22) column 1, line 46-57 column 2, line 44-48 column 4, line 42,43 column 6, line 5-28 column 6, line 61 -column 7, line 6 ----	1-30
A	US 4 366 128 A (WEIR DONALD R ET AL) 28 December 1982 (1982-12-28) claim 1 column 1, line 27-35 column 2, line 19-31 ----	22
A	US 5 173 194 A (HERING JR CARL J) 22 December 1992 (1992-12-22) figure 1 -----	23,28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/40056

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 471277	A	01-09-1937	NONE	
US 6132623	A	17-10-2000	US 6387276 B1 AU 8259098 A CA 2293656 A1 EP 0991595 A1 WO 9857893 A1	14-05-2002 04-01-1999 23-12-1998 12-04-2000 23-12-1998
DE 2724254	A	09-11-1978	DE 2724254 A1	09-11-1978
US 6426005	B1	30-07-2002	AU 4896201 A AU 754359 B2 AU 5545701 A BR 0106070 A CA 2376616 A1 CN 1380835 T EP 1229980 A2 NO 20016142 A WO 0178864 A1 WO 0179117 A2	30-10-2001 14-11-2002 30-10-2001 14-05-2002 25-10-2001 20-11-2002 14-08-2002 17-12-2001 25-10-2001 25-10-2001
US 4126546	A	21-11-1978	US 4197201 A	08-04-1980
US 5369072	A	29-11-1994	US 5911882 A	15-06-1999
US 3499837	A	10-03-1970	NONE	
US 6468942	B1	22-10-2002	AU 3766102 A CA 2429510 A1 EP 1341970 A2 WO 0244088 A2 US 2002090261 A1	11-06-2002 06-06-2002 10-09-2003 06-06-2002 11-07-2002
US 4366128	A	28-12-1982	CA 1139466 A1 AU 542073 B2 AU 7315981 A DE 3132126 A1 FR 2488869 A1 GB 2082564 A ,B JP 1003550 B JP 1526029 C JP 57059686 A ZA 8105308 A	11-01-1983 07-02-1985 25-02-1982 08-04-1982 26-02-1982 10-03-1982 23-01-1989 30-10-1989 10-04-1982 25-08-1982
US 5173194	A	22-12-1992	NONE	